Despite the uncertain relationship of the earlier work to ours, the evidence presented in this paper strongly supports assignment of α- and β-Co(tetren)-Cl^{2+} to configurations I and II, respectively.

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Nuclear Magnetic Resonance Study of Some Cobalt(III) Complexes with Known Chelate Ring Conformations[1,2]

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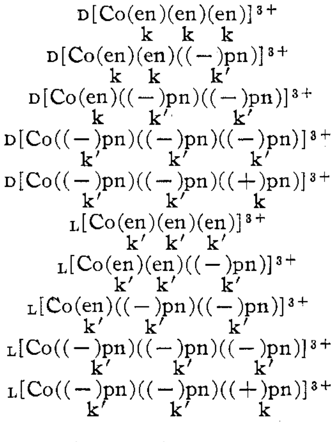
The nmr spectra of some cobalt(III) 1,2-diaminoethane (en) and/or 1,2-diaminopropane (pn) complexes are recorded. Although the chemical shift for each different kind of hydrogen is easily determined, the fine structure is not sufficiently well resolved to allow unambiguous assignments to be made for the different conformations of the individual chelate rings; however, the spectra support the interpretation of previous thermodynamic data. The chemical shifts for N–H protons are quite large and are rationalized in terms of the effective field for each proton in relation to the stereochemistry of the ion.

Introduction

High-resolution proton magnetic resonance spectroscopy has shown its ability to provide information about the structures of a variety of organic compounds but only a few papers have been concerned with its application to metal complexes.[3–11] We were interested in using this tool to examine the possibility of detecting ligand conformational isomers in complexes where en or similar ligands were coordinated. These chelate systems are somewhat analogous to the cyclopentane structure in that they are known to be nonplanar[12,13] and therefore can exist in two mirror-image forms as shown in Figure 1.

In some complexes of this nature the stereochemical details are known reasonably well, *e.g.*, D- and L$[\mathrm{Co(en)_3}]^{3+}$, -$[\mathrm{Co(en)_2((-)pn)}]^{3+}$, -$[\mathrm{Co(en)((-)pn)_2}]^{3+}$, and -$[\mathrm{Co((-)pn)_3}]^{3+}$,[14–16] and the relative thermodynamic stabilities of the ions can be rationalized in terms of nonbonded interactions between the atoms in the different conformations as described by Corey and Bailar.[17] In fact, there is such good agreement between theory and experiment that these compounds would seem to be good models for determining the conformations of rings in other similar systems using the nmr technique.

The stability differences observed[14,15] imply the following conformations in the en and pn rings



$$\mathrm{D}[\mathrm{Co}\underset{k}{(\mathrm{en})}\underset{k}{(\mathrm{en})}\underset{k}{(\mathrm{en})}]^{3+}$$
$$\mathrm{D}[\mathrm{Co}\underset{k}{(\mathrm{en})}\underset{k}{(\mathrm{en})}\underset{k'}{((-)\mathrm{pn})}]^{3+}$$
$$\mathrm{D}[\mathrm{Co}\underset{k}{(\mathrm{en})}\underset{k'}{((-)\mathrm{pn})}\underset{k'}{((-)\mathrm{pn})}]^{3+}$$
$$\mathrm{D}[\mathrm{Co}\underset{k'}{((-)\mathrm{pn})}\underset{k'}{((-)\mathrm{pn})}\underset{k'}{((-)\mathrm{pn})}]^{3+}$$
$$\mathrm{D}[\mathrm{Co}\underset{k'}{((-)\mathrm{pn})}\underset{k'}{((-)\mathrm{pn})}\underset{k}{((+)\mathrm{pn})}]^{3+}$$
$$\mathrm{L}[\mathrm{Co}\underset{k'}{(\mathrm{en})}\underset{k'}{(\mathrm{en})}\underset{k'}{(\mathrm{en})}]^{3+}$$
$$\mathrm{L}[\mathrm{Co}\underset{k'}{(\mathrm{en})}\underset{k'}{(\mathrm{en})}\underset{k'}{((-)\mathrm{pn})}]^{3+}$$
$$\mathrm{L}[\mathrm{Co}\underset{k'}{(\mathrm{en})}\underset{k'}{((-)\mathrm{pn})}\underset{k'}{((-)\mathrm{pn})}]^{3+}$$
$$\mathrm{L}[\mathrm{Co}\underset{k'}{((-)\mathrm{pn})}\underset{k'}{((-)\mathrm{pn})}\underset{k'}{((-)\mathrm{pn})}]^{3+}$$
$$\mathrm{L}[\mathrm{Co}\underset{k'}{((-)\mathrm{pn})}\underset{k'}{((-)\mathrm{pn})}\underset{k}{((+)\mathrm{pn})}]^{3+}$$

The k conformation of the chelate ring has the C–C bond roughly parallel to the threefold axis in the D complexes and the same situation exists for the k′ conformers in the L complexes. While the en rings change conformations when going from D to L the (−)pn rings do not because the requirement for the methyl group to be always equatorial makes one conformer more stable regardless of the absolute configuration of the complex. The energy difference between the conformers with the methyl group in the axial and equa-

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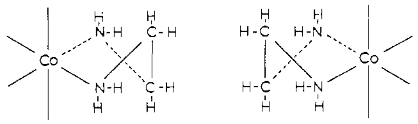

Figure 1.—Mirror image forms of the Co(en) chelate ring.

torial positions has been estimated to be 2–3 kcal/mole[17] and this is enough to ensure that >95% of the ligand is in the form with CH_3 equatorial. This is significant because in L[Co((−)pn)$_2$((+)pn)]$^{3+}$ two different conformations appear in the same ion and both forms are stabilized by the methyl groups. A similar situation arises with D[Co(en)$_2$((−)pn)]$^{3+}$ except that the en conformations may not be stabilized to the same extent. These considerations apply to the equilibria involved and do not necessarily indicate how rapidly conformational interchange can take place.

The spectra and results of this investigation are given below.

Experimental Section

Preparation of Compounds.—The compounds were prepared as described in the literature[14,15] and were analytically and optically pure.

Nmr Measurements.—The spectra reported here were recorded on a Varian HR-100 spectrometer. Similar results were obtained on a Varian A-60 instrument but with less resolution. All spectra were run in D_2O or mixed D_2O–D_2SO_4 solutions (*ca.* 5–15 wt % complex) and chemical shifts were measured relative to tetramethylsilane as an external reference. The chemical shifts have not been corrected for the diamagnetic contributions of the complexes or solvents and the HOD signals have been omitted in Figures 2–4.

The presence of D_2SO_4 slows the rate of deuteration of the NH_2 groups ($t_{1/2}$ > 2 days in 1 *M* D^+) as the rate of exchange of D for H is inversely proportional to [D^+].[18] The position of the HOD resonance is strongly dependent upon the acid concentration and therefore is not reported. The positions of the other peaks, with the exception of a small variation in the NH region, were unaffected by changing the acid concentration. In D_2O alone the NH_2 groups were rapidly deuterated and the N–H signal disappeared so that the N–H and C–H resonances were easily distinguished.

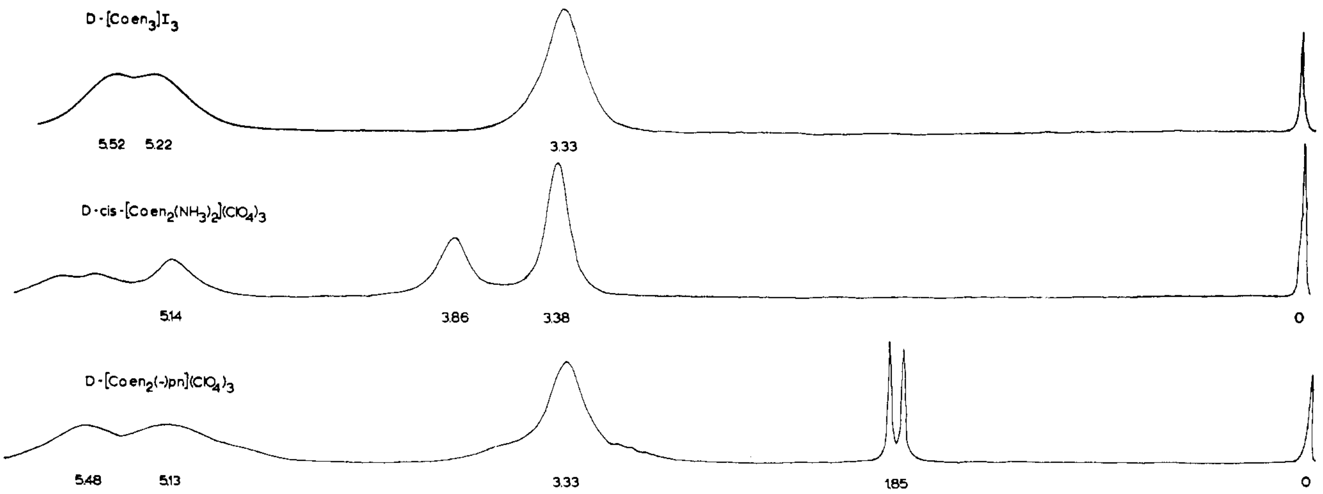

Figure 2.—Nmr spectra of typical Co(III) complexes.

Results and Discussion

While the proton resonances associated with NH_2, CH, CH_2, and CH_3 groups were easily identified, the interpretation of each region in terms of the possible conformers was more difficult. The methyl group gave a sharp doublet split by 6 cps, which is characteristic of a secondary methyl group. The $-CH_2$-CH_2- and $-CHCH_2-$ regions were broad and poorly resolved, and the NH_2 resonances were also broad. The spectra are shown in Figures 2 and 3. Also, the $-CH_2CH_2-$ peak for [Co(en)$_3$]$^{3+}$ was unresolved down to −39° and deuteration of the NH_2 groups did not affect the band greatly. (A decrease in half-width from 21 to 18 cps was observed.) This agrees with the observations of Powell and Sheppard[7] and is not inconsistent with their proposal that the broadening may be due to the interaction of these protons with the spin of $^7/_2$ on the cobalt nucleus.

It is not surprising the $-CH_2CH_2-$ and $CH_3(CH)$-CH_2- regions are broad. The former system in the *gauche* form could give rise to an A_2B_2 pattern (24 lines) providing all three ligands held the same conformation. If the (+)[Co(en)$_3$]$^{3+}$ ion, for example, exists partly in the kkk′ form, as seems likely, then the D_3 symmetry is destroyed and the spectra arising from the three ligands are no longer equivalent but overlap and the result is even more complicated.

Similarly the CH of the >$CHCH_3$ grouping could lead to a 16-line spectrum irrespective of combination lines. As this pattern overlaps the spectrum arising from the $-CH_2CH_2-$ groups it is not surprising that fine structure is not observed in the mixed en and pn compounds. In addition, these remarks ignore any coupling between C–H and N–H which would lead to an even greater complexity. In the systems which show D_3 symmetry in solution, L[Co((−)pn)$_3$]$^{3+}$, all methyl groups are *cis*[13] and the ligands are in the same conformations k′. Some fine structure did emerge in the –CH– region of these compounds, Figure 4.

On the other hand if the conformational interchange

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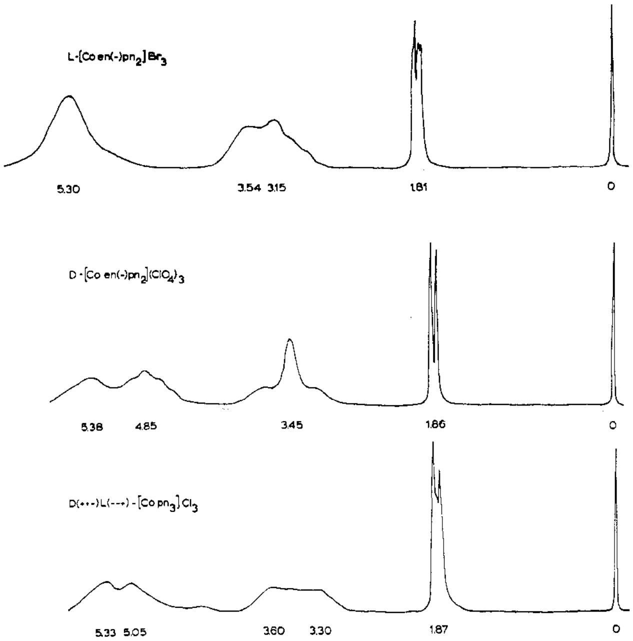

Figure 3.—Nmr spectra of mixed en–pn Co(III) complexes.

TABLE I

CHEMICAL SHIFTS IN SOME COBALT(III) COMPLEXES[a]

Complex	$\delta(NH_2)$	$\delta(CH)$	$\delta(CH_2)$	$\delta(CH_3)$
L$[Co(en)_2((-)pn)]Cl_3$	5.35	3.60	3.29	1.85
L$[Co(en)((-)pn)_2]Br_3$	5.30	3.54	3.15	1.81
L$[Co((-)pn)_3]Cl_3$	5.30	3.52	2.93	1.87
D$[Co(en)_2((-)pn)](ClO_4)_3$	5.48, 5.13		3.33	1.85
D$[Co(en)((-)pn)_2](ClO_4)_3$	5.38, 5.00		3.45	1.86
D$[Co((-)pn)_3]Cl_3$	5.63,	3.64	3.13	1.85
D$(++-)$L$(--+)[Co(pn)_3]Cl_3$	5.33, 5.05	3.60	3.30	1.87
D$[Co(en)_3]I_3 \cdot H_2O$	5.52, 5.22		3.33	

[a] Measured in ppm with tetramethylsilane as an external reference. All spectra were run in mixed D_2O–D_2SO_4 solutions (approximately 1 M D^+). The NH_2 groups are deuterated in D_2O alone.

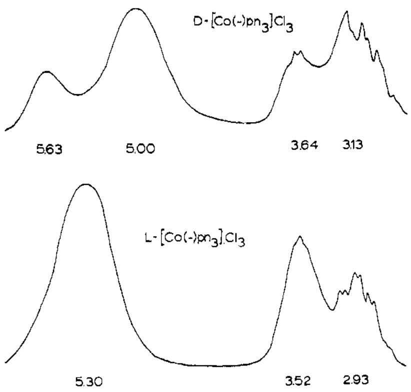

Figure 4.—Expanded spectra in NH, CH, and CH_2 regions for D- and L$[Co((-)pn)_3]Cl_3$.

is rapid enough (>100 sec^{-1}) only a single sharp line would be expected in the $-CH_2CH_2-$ and sharper lines for the $CH_3(CH)CH_2-$ regions, possibly somewhat broadened by coupling with the protons on nitrogen. Deuteration of the NH_2 groups did sharpen the C–H regions but the bands were still broad. This may mean that the conformations are retained or it may indicate that the interchange occurs at an intermediate rate. Variable temperature studies are in progress to check this latter possibility.

Despite the lack of information for the CH regions, the N proton shifts were large in some instances and revealing in terms of the structure of the ion. The chemical shifts for the N proton resonances in *cis* and *trans* $-[Co(en)_2(NH_3)_2]^{3+}$ were rationalized as follows. The band at 3.50 ppm in the *trans* complex was attributed to both NH_3 and CH_2 protons and the band at 5.30 ppm to the symmetrical NH_2 groups assuming there was rapid interchange of the conformers. The peak areas were consistent with this view and deuteration decreased the intensity of the superimposed NH_3 and $-CH_2CH_2-$ signals as expected and eliminated that due to the NH_2 groups.

For the *cis* ion the band at 3.86 ppm (6 protons) was assigned to the NH_3 groups and the bands at 5.14 (4), 5.50 (2), and 5.67 ppm (2) were attributed to the nonequivalence of the NH bands with respect to the symmetry of the molecule. The orientation is described in terms of the nearest N protons. The effects of the CH interactions on the NH resonances are omitted although they must contribute to the field. The ion has a twofold axis of symmetry, and for the NH_2 groups *trans* to one another, the four hydrogens see essentially the field due to the two NH_3 groups. Similarly, the NH_2 groups *cis* to one another are symmetrically placed but the pairs of protons see different fields, one pair is shielded by one NH_3 group and one NH_2 group while the other pair sees two NH_2 groups. The peak areas are in the ratio of 4:2:2 and it is proposed that these peaks are due to: (1) the four hydrogens in the *trans* NH_2 groups, (2) the two hydrogens adjacent to one NH_3 group and one NH_2 group, and (3) the two hydrogens adjacent to two NH_2 groups. This assignment is reasonable if the NH_2 group shields the contiguous protons more than the ammonia group.

In all the complexes containing pn the CH_3 doublet occurred at approximately the same frequency (1.85 ppm) and was split by 6 cps. Recently, Woldbye and co-workers[19] measured the proton nmr spectrum of $[Co(\textit{meso}\text{-}2,3\text{-diaminobutane})_3]^{3+}$ in D_2O and found two doublets of equal intensity corresponding with δ values of 1.73 and 1.85 ppm. In this instance the staggered conformation of the ring requires one methyl group to be axial and the other equatorial. It would seem then that the doublet at 1.85 ppm is characteristic of the equatorial methyl group. This was verified by the spectrum of $[Co(d\text{-}2,3\text{-diaminobutane})_3]^{3+}$ which gave only one doublet at 1.85 ppm and is consistent with the observation that axial substituents absorb at higher frequencies than the equatorial substituents in substituted cyclohexanes.[20]

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